

A STUDY OF THE EFFECTS OF RESORCINOL  
ON THE VAPOR-LIQUID EQUILIBRIA  
OF THE SYSTEM PARAXYLENE - ORTHOXYLENE

by

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## SUMMARY

Vapor liquid equilibrium data were determined for the system, paraxylene - orthoxylene and for the system, paraxylene - orthoxylene - resorcinol. The effects of resorcinol on the separation of the two xylene isomers was determined. A method was devised for analyzing samples of the vapor and liquid equilibrium compositions.

A curve from which compositions of xylene solutions could be read with known refractive indices was determined. Equilibrium data were determined with an Othmer still for the system, paraxylene - orthoxylene. A Hands and Norman still was used to determine equilibrium data for the three component system which included the two xylenes and resorcinol. Resorcinol concentrations in the liquid phase were 20, 40, and 90 per cent of the total weight.

The results show that the resorcinol is selective to o-xylene. The relative volatility of p-xylene to o-xylene is increased with increased concentrations of resorcinol in the liquid phase. However, increased concentrations of resorcinol above forty per cent do not have as much effect as increases in concentration up to forty per cent. This is so pronounced that a concentration of resorcinol in the vicinity of forty per cent would probably be the maximum practical concentration in a distillation system.



## INTRODUCTION

Many methods have been devised to separate the three xylene isomers to their pure state. All of the known methods are expensive, and the cost of the isomers in their pure state is very high. Separation of these compounds, m-xylene, p-xylene, and o-xylene is very difficult because of the similarity of their structures, and of their physical properties. Table XI contains the physical properties of these compounds in tabular form. The problem of this study is to explore the possible use of resorcinol as an extractive agent for use in extractive distillation of paraxylene and orthoxylene.

The demand for each isomer in its pure form has been increasing and the demand will increase more rapidly if the cost of the pure substances can be reduced.<sup>1</sup> Most of the xylene produced today is used in gasoline blends. However, the o-xylene is detrimental to the blend. If this compound could be removed from the mixture, the two remaining isomers would make a blending agent superior to the mixture of three xylenes. The extracted ortho isomer has an important use in the production of phthalic anhydride. Previous to 1945 this anhydride was produced exclusively from naphthalene. P-xylene is used in the production of Dacron for forming the compound terephthalic acid. The para isomer is also important for the production of Mylar, a film base.

Three important methods of separation are (1) distillation, (2) selective sulfonation, and (3) selective crystallization. It is possible to separate o-xylene from the other

two xylenes by ordinary distillation. However, a distillation column of many plates is required for the separation. If advantage is taken of the slight increase in relative volatility at low pressures a distillation column with a very large diameter may be required for the separation. Selective sulfonation<sup>6</sup> has been used for many years to separate the meta compound from its isomers, orthoxylene and paraxylene. This reaction is successful because the rate of sulfonation of m-xylene is faster than for the other compounds. The faster hydrolysis of m-xylene sulfonate also aids the usefulness of this reaction. The third method of separation mentioned is selective crystallization. The melting point of p-xylene is 13.3° C., while those for o-xylene and m-xylene are minus 25° and minus 47.7° respectively. This difference in melting points is a great aid to the crystallization of p-xylene from a mixture of xylenes. A eutectic is formed,<sup>6</sup> however, which limits the recovery of p-xylene to 50 per cent of the para present.

The point of view of the author in this work is that of reducing the cost of separation of o-xylene from the meta and para compounds by distillation. If the proper substance were added to the distillation system as an extractive agent the required size of the distillation column could be reduced considerably. The problem was approached from the standpoint of separating o-xylene from p-xylene. This was done chiefly because of the difficulties involved in analyzing a mixture of all three xylenes. It was hoped that if an extractive agent was more selective to the ortho compound with respect

to the para isomer that it would also be more selective to the ortho than to the meta compound.

In the sections following an attempt has been made to outline the problem and to describe the procedure used in doing this work. A section is devoted to the results and a brief outline of what they mean. The possible use of the data collected and future work to be done are discussed.

## STATEMENT OF PROBLEM

1. Devise a method of analyzing two and three component systems.
2. Determine vapor-liquid equilibrium data for system para-xylène and orthoxylene.
3. Determine vapor-liquid equilibrium data for system para-xylene, orthoxylene and resorcinol.

## MATERIALS USED

Orthoxylene:

Orthoxylene with a B. P. range of 143.5-144.5° C. was obtained from the Matheson Company, Inc. (Chemical No. 5819). It was used directly for refractive index determinations and for the vapor-liquid equilibrium determinations of the two component system. For later runs a compound of 99.0 mole per cent minimum purity was obtained from Phillips Petroleum Co. for use. An attempt was made to purify this ortho isomer further with a true boiling point still which has one hundred theoretical trays. The refractive index of the product indicated there was no change in the composition. This chemical was mixed with some of that obtained from the Matheson Co.

Paraxylene:

Paraxylene with a M. P. range of 12-13° C. was obtained from the Matheson Company, Inc. (Chemical No. 5821). It was used directly for refractive index determinations and for the vapor-liquid equilibrium determinations of the two component system. For later runs paraxylene obtained from Eastman Kodak Company was used. This chemical was mixed with some obtained from the Matheson Company.

Resorcinol:

Resublimed resorcinol of C. P. grade was obtained from the Matheson Company, Inc. (Chemical No. 2869). This substance had a melting point range of 109 - 111° C. The original resorcinol was tested for purity by U. S. P. standard

tests (see page 48). However, the chemical discolors with use due to exposure to light and to air. No attempt was made to recover the resorcinol to its pure form after usage.

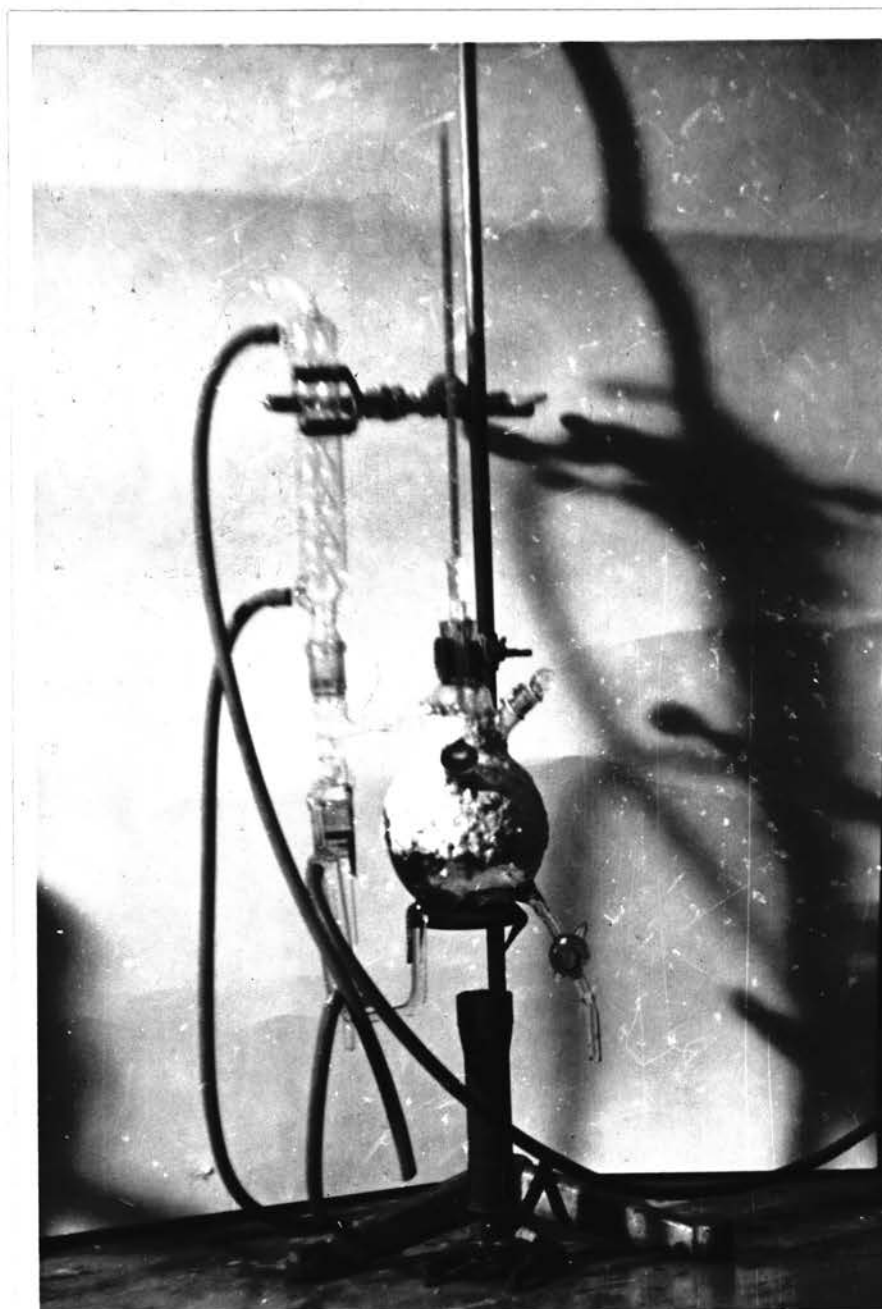
## APPARATUS AND INSTRUMENTS

Othmer Still:

An Othmer type still was used for the two component,<sup>7,8</sup> single liquid phase runs. This still is shown in Figure 1. It is a continuous distillation apparatus which is constructed to minimize fractionation of the vapors leaving the liquid phase. The still has a glass tube projecting down into the still pot. This tubing is a passage way for the vapor sample and is kept hot by vapors around it in the still pot. Vapor is thus kept from condensing on the inside and from causing a wetted wall column effect. The still has a vapor sample space with an overflow tube which returns condensed vapors to the still pot. When equilibrium is obtained, the composition of this overflow is the same as the vapors leaving the still pot. The composition of the liquid does not change as distillation progresses. Pressure is maintained constant in the still by connecting a constant pressure source to the top of the condenser. The pressure regulator used was a Cartesian Industrial Manostat. The manostat used a compressed air line as its source of pressure. A water filled manometer was used to check the still pressure with atmospheric pressure. One leg of the manometer was open to the atmosphere and the other leg was connected to the system. A line drawing of the system is shown in Figure 4.

FIGURE 1

VIEW OF OTHMER STILL





### Hands and Norman Still:

A Hands and Norman still was used for the three component, two liquid phase systems.<sup>4</sup> This still is shown in Figure 2. This still has a concentric tube which projects down the length of the flask neck. Vapors in the annular space prevent condensation from taking place within the tube. The vapors for the sample pass up through this tube and over to a vertical condenser. At the base of this condenser is a two-way stopcock which recycles condensed vapors back to the pot, or collects condensed vapors when shut off, or passes the condensed vapors into the atmosphere. This last position is used to take a sample for analysis. The still is a dynamic distillation apparatus and has the disadvantage of error in the liquid composition. The composition of the liquid changes as the vapor sample is collected. This change in composition is small for large amounts of liquid but is considerable when small amounts of liquid are used. The advantage of using this still over that of using the Othmer still for this work is that this still has no tubing connected to the bottom of the still pot. In the Othmer still, the heavier resorcinol layer would solidify in the low sections of the tubing. The Hands and Norman still has a device which helps prevent vapors from condensing inside the tube in the neck of the flask. A condenser is attached at the top of the annular space to allow hot vapors to pass all of the way up the neck before they condense. The reflux from the condenser passes back down the annulus to the still pot. The hot vapors in the annulus help

FIGURE 2

VIEW OF HANDS AND NORMAN STILL  
AND AUXILIARY APPARATUS



to form an adiabatic column for the vapors in the tubing. Insulation around the neck of the still flask also aided the formation of an adiabatic column. The constant pressure source was connected at the top of the reflux condenser. The Cartesian Manostat and the manometer were used as with the Othmer still.

#### Abbe Refractometer:

An Abbe Refractometer<sup>2</sup> was used to determine the refractive indices of the xylenes. However, there are two reasons for not using this instrument for the analytical work. First, its precision can only be certain at  $\pm 0.0002$  index units. Since the difference between the refractive indices of the two xylenes was only 0.0077, observed compositions could have an error of 2.6 per cent induced by the index readings alone. The second disadvantage for this work is the fact that the Abbe Refractometer uses only a few drops of liquid for reading. Since the xylenes are quite volatile, error could be introduced by evaporation of the sample before the prisms were closed and readings taken.

#### Zeiss Dipping Refractometer:

A Zeiss dipping refractometer<sup>2</sup> was used for the analysis of liquid and vapor samples. This instrument uses from five to ten milliliters of liquid into which a prism is immersed. Vials, containing the samples, were immersed in a constant temperature trough which was constructed for use with the Zeiss Refractometer. A support held the refractometer in position so that the glass prism at its base was suspended

in the vials at the correct angle to receive light which passed up through an aperture on the bottom of the trough and through the liquid sample in the vial. A field of vision with a scale numbered from zero to one hundred is seen when looking into the top of the instrument. The instrument has several detachable prisms which connect at the base. Each prism covers a small range of refractive index units. For this reason precision is carried out to the fifth decimal place of refractive index. The difference between readings for the two xylene isomers is about 25 units on the scale. Each unit can be read accurately to the tenth of a unit, the uncertainty being in the hundredth decimal. The error in reading is reduced to 0.4 per cent with this instrument. Error due to evaporation of the samples is reduced to a minimum because of the comparatively large sample used. The instrument does take longer to give correct readings because there is more liquid to reach the temperature of the bath. Also, the constant temperature bath is more affected by room temperature because of the large volume of water in the trough at all times. Cooling water for the bath had to be refrigerated during the hot summer days because tap water was at a higher temperature than that desired. The refractometer is pictured in Figure 3 along with the constant temperature control. Figure 5 is a line drawing of the system shown in the photograph.

FIGURE 3

VIEW OF ZEISS REFRACTOMETER AND  
TEMPERATURE CONTROL EQUIPMENT

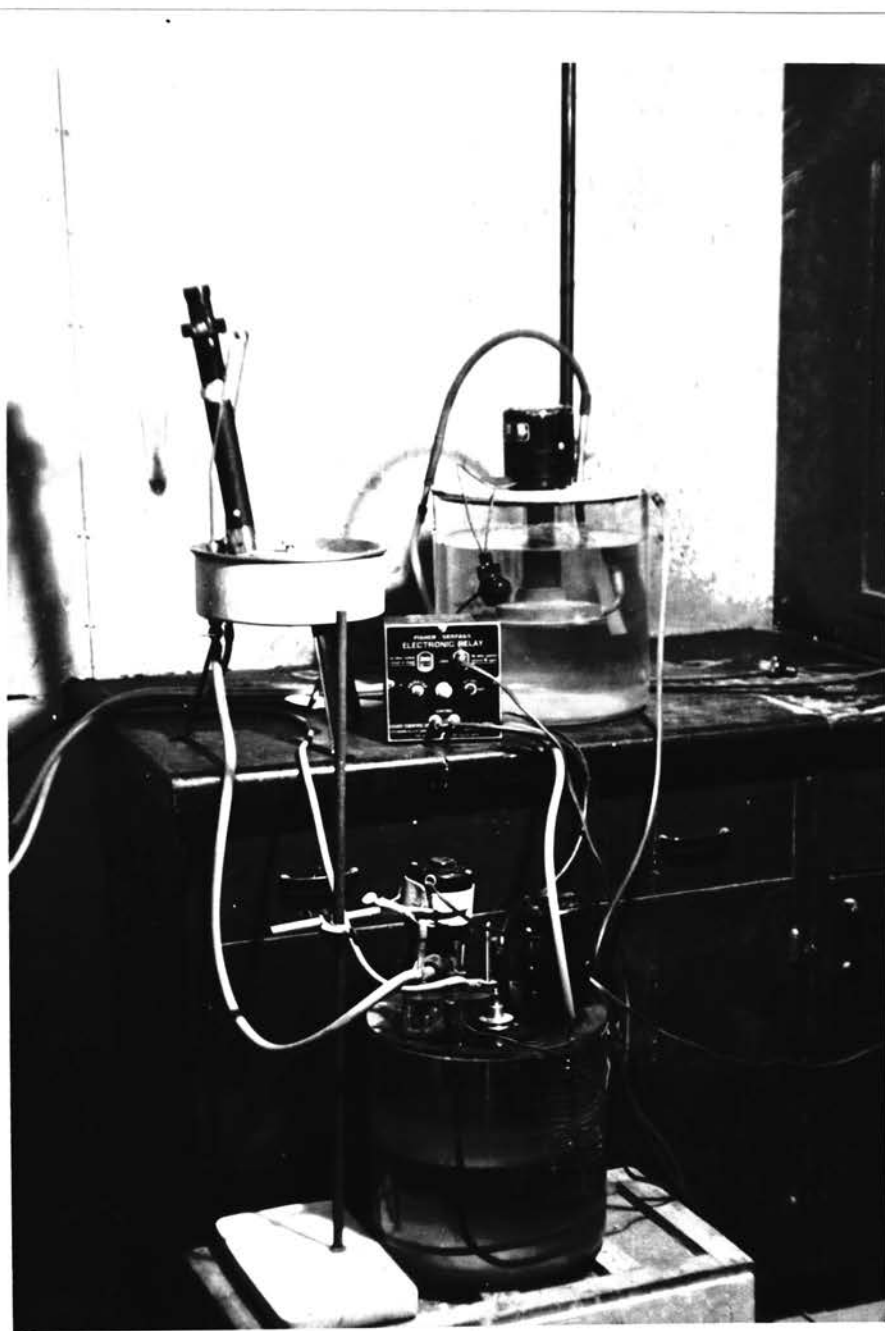


FIGURE 4  
 LINE DRAWING OF STILL  
 AND AUXILIARY APPARATUS

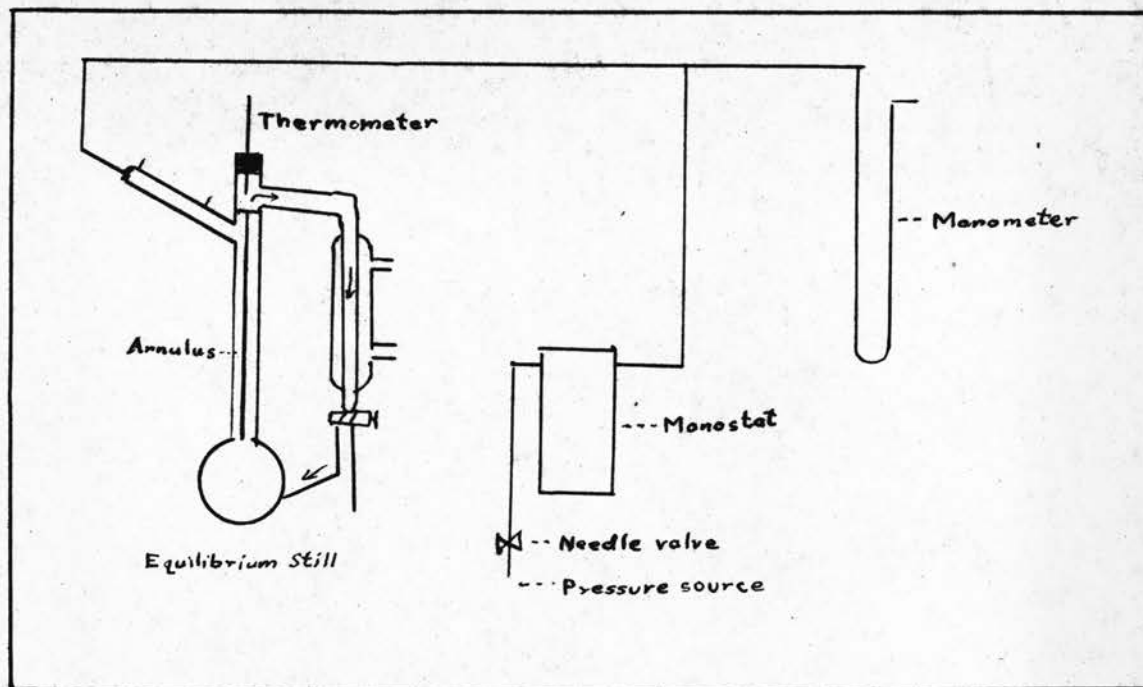
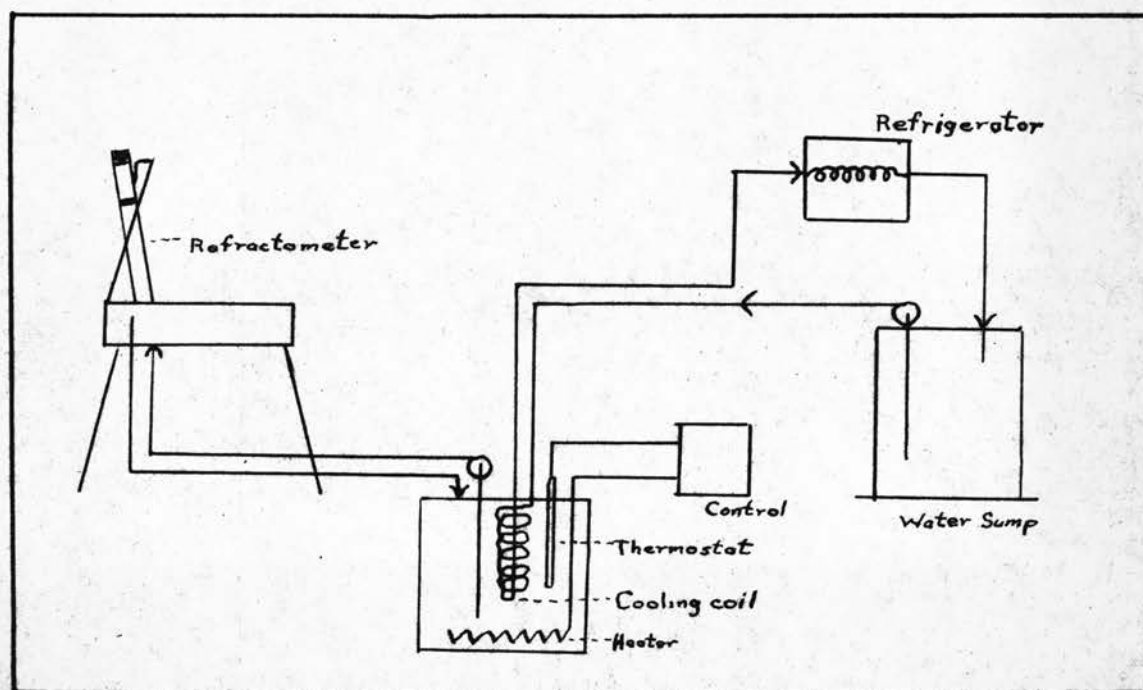


FIGURE 5  
 LINE DRAWING OF REFRACTOMETER AND  
 TEMPERATURE CONTROL EQUIPMENT



## PROCEDURE

Analytical:

## (Two Component System)

The method used for analyzing mixtures of p-xylene and o-xylene was that of refractive index determination. The Abbe Refractometer was used to determine the refractive index of mixtures of the isomers in known proportions at 25° C. Table III is the tabulated data for refractive index and per cent p-xylene in the solution. Figure 6 is a plot of these results. Values of refractive index for the isomers were found in the literature and a comparison of these with the author's values is made in Table I. The author's value for o-xylene is favorable while the value for p-xylene is quite low as compared with the values found in the literature.

TABLE I

Refractive Indices of Paraxylene -  
Orthoxylene at 25° C.

---

	This Work	Literature	
o-xylene	1.5008	1.50282	(Forziati, 1946)
p-xylene	1.4931	1.49319	(Forziati, 1946)

For this analysis work a Zeiss dipping refractometer was used. A brief description of this instrument is given on page 12. This instrument had to be calibrated for refractive index and for per cent p-xylene in the mixture. These results are tabulated in Table IV and plotted in Figures 7 and 8 respectively. The temperature at which these values were

FIGURE 6

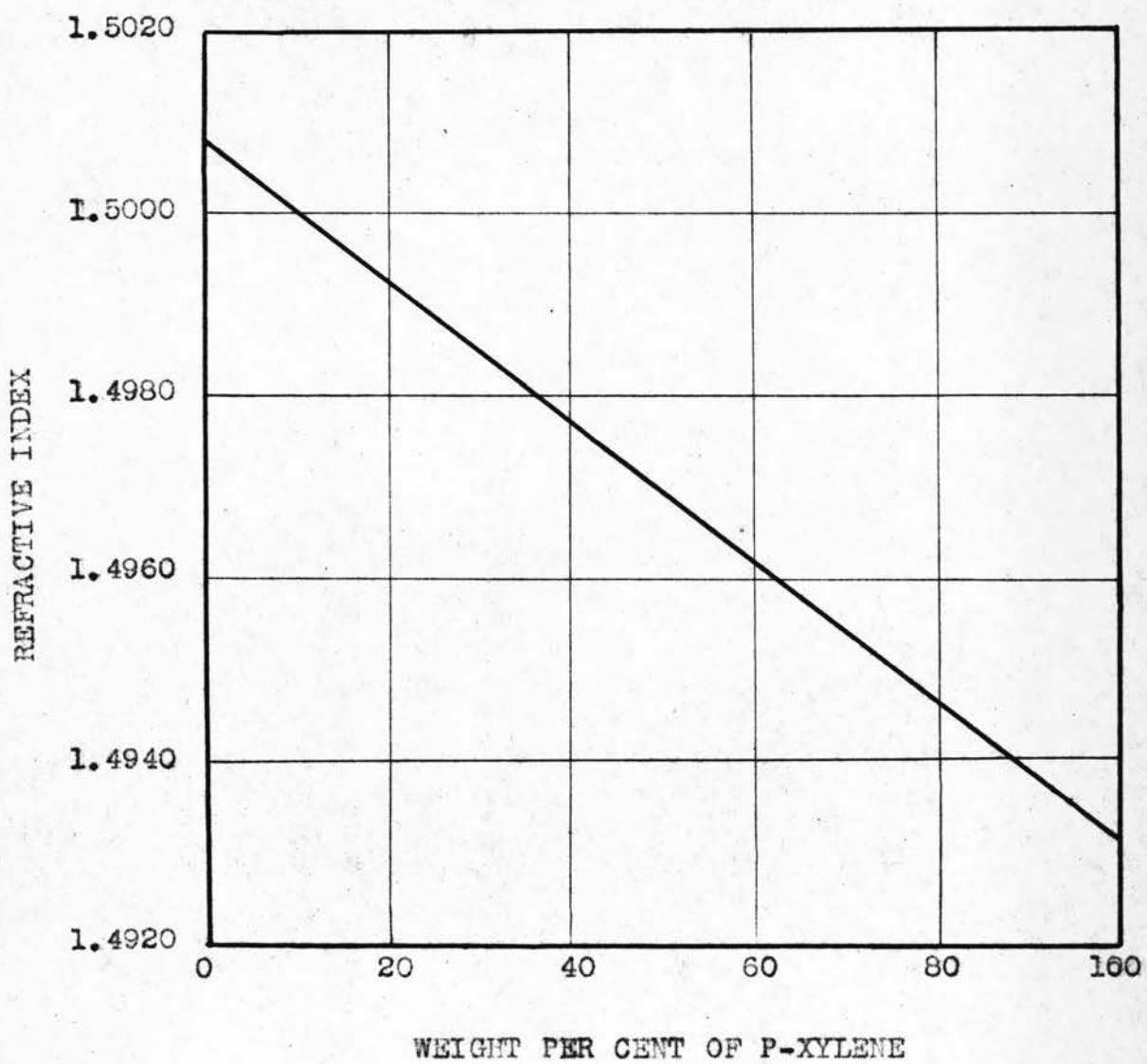
REFRACTIVE INDEX OF O-XYLENE AND  
P-XYLENE SOLUTIONS AT 25° C.



FIGURE 7

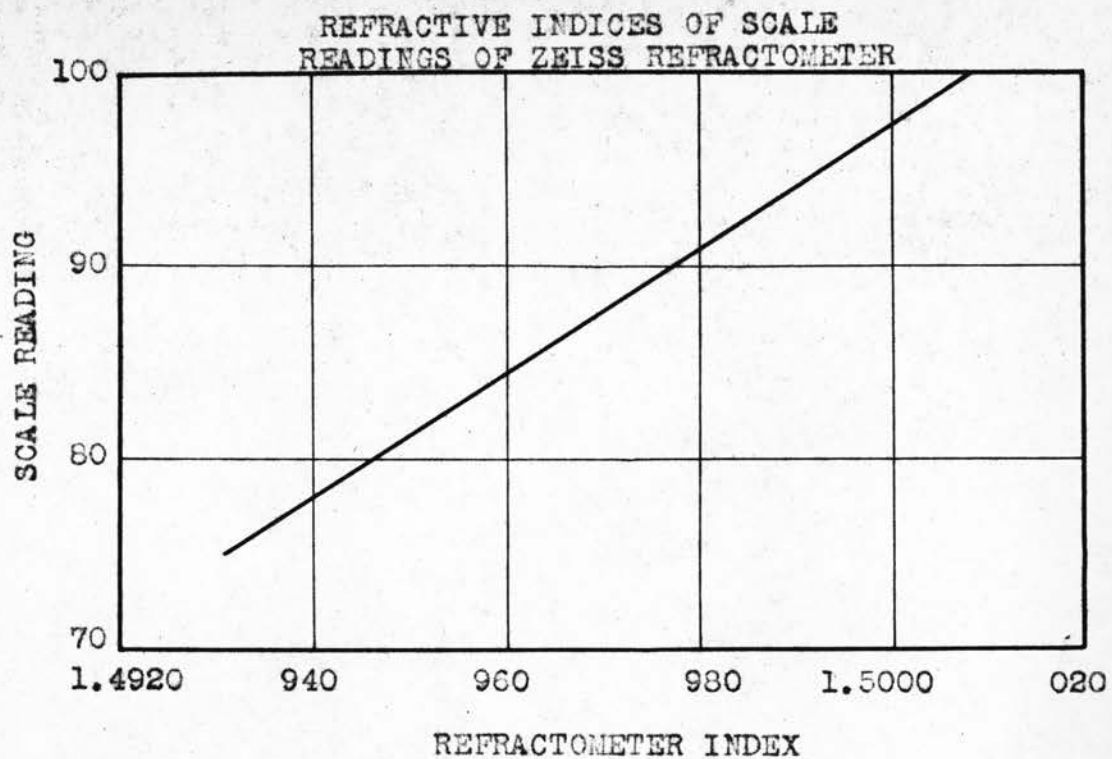
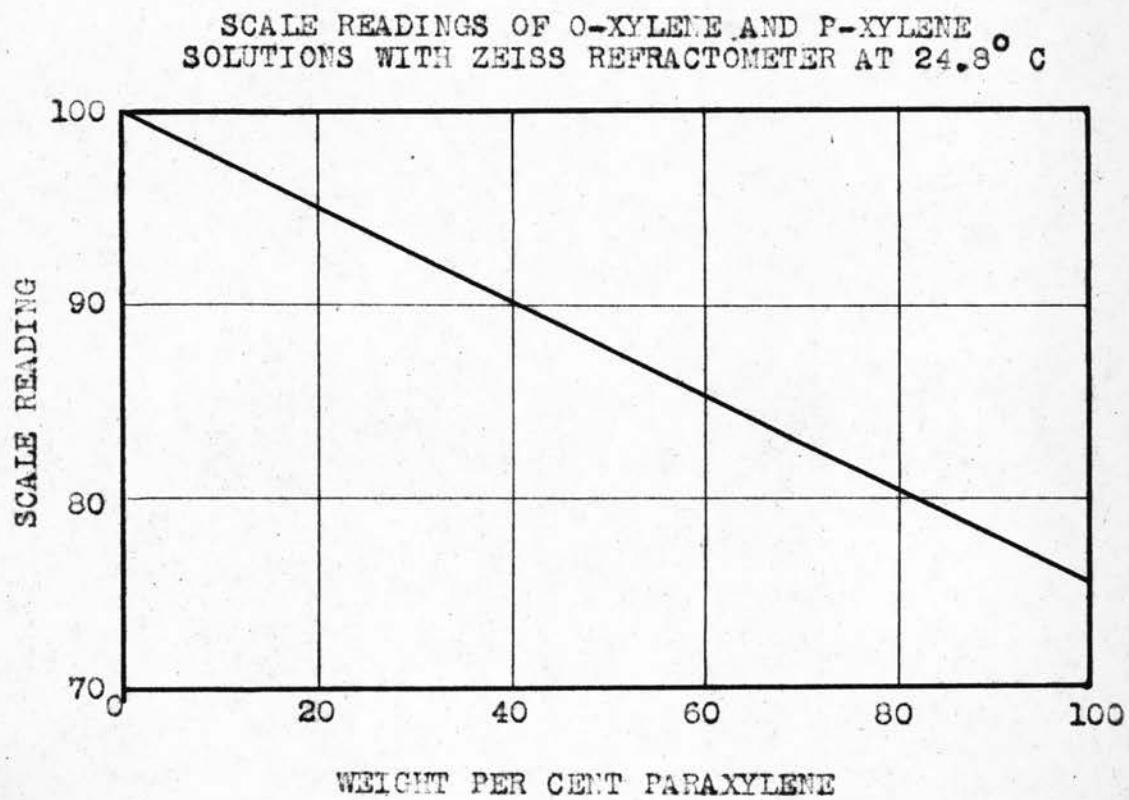


FIGURE 8



determined was  $24.8^{\circ}$  C. This temperature was measured with a Zeiss thermometer which was calibrated with a standard Bureau of Mines thermometer.

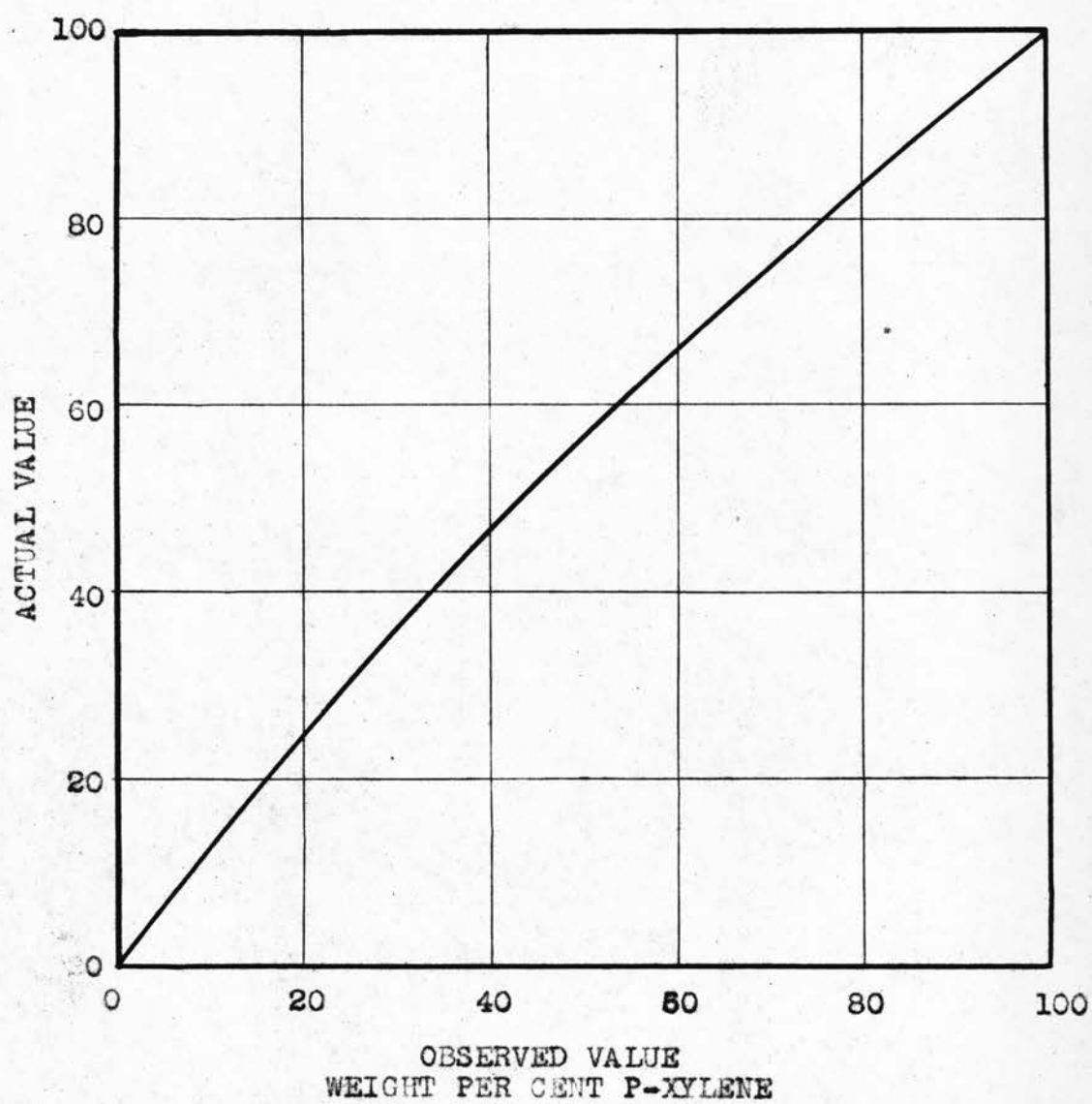
(Three Component System)

The analysis of samples for the three component system with 20 and 40 per cent concentrations of resorcinol was much the same as that for the two component system. No detectable amount of resorcinol was found in the vapor samples. The liquid sample of xylenes was decanted from the still after it cooled to room temperature. Tests showed that the resorcinol was less than 0.25 per cent soluble in the xylenes at  $25^{\circ}$  C. There was no difference in the refractive indices of the pure xylenes and of those xylenes saturated with resorcinol. However, the samples decanted from the still proved to have different compositions than the actual overall compositions of the resorcinol-free xylenes in the still. Tests were run by heating mixtures of resorcinol and known concentrations of xylenes to boiling and then allowing the mixtures to cool. The xylene was then decanted. In every case this decanted mixture of o-xylene and p-xylene had a lower concentration of the para isomer than did the original mixture. The actual composition of the resorcinol-free liquid is plotted against values of observed readings in Figure 9. These values are tabulated in Table V.

The analysis of the liquid and vapor in equilibrium for the three component system with 90 per cent resorcinol in the liquid phase was made in a very different manner. Since

FIGURE 9

DEVIATIONS OF OBSERVED COMPOSITIONS  
FROM ACTUAL COMPOSITIONS IN LIQUID  
PHASE OF THE THREE COMPONENT SYSTEM



liquid xylene could not be separated from the resorcinol after cooling, the composition in the liquid phase was calculated. The vapor samples still had no detectable amount of resorcinol in them. The vapor samples were weighed and analyzed. An amount of pure xylene equal to this sample was added to the still. The composition of the resorcinol-free xylenes changed as the vapor sample was collected. The beginning and end compositions were calculated and an average of the two values was used for determining vapor-liquid equilibrium.

Operational Technique:

(Othmer Still)

The Othmer equilibrium still was used for determining vapor-liquid equilibrium data for the paraxylene - orthoxylene system. This still could not be used for the systems containing resorcinol because the resorcinol solidified in the lower section of the recycle tube. The still was charged with approximately 350 gm. of xylenes. The Cartesian Manostat was adjusted to hold the pressure in the still at 760  $\pm$  2.5 mm. Hg. A Fisher burner was used to produce heat for the still. After condensed vapors started to return to the still the flame was adjusted to a height that would boil the liquid at a rate of sixty drops per minute. The still was then allowed to reach equilibrium. Samples of condensed vapors and of the liquid were then removed for analysis. The time required for the still to reach equilibrium was determined by removing vapor samples at fifteen minute intervals from forty-five minutes to one hour and fifteen minutes. The results agreed

closely. One hour of boiling was therefore considered sufficient. Table II has tabulated results for this test.

TABLE II  
The Boiling Time Required for  
Equilibrium to be Obtained  
In Othmer Still

<u>Time (Min.)</u>	<u>% P in Liquid</u>	<u>% P in Vapor</u>
45	21.4	25.5
60	21.1	25.5
75	20.3	24.4

(Hands and Norman Still)

A Hands and Norman still was used to determine vapor-liquid equilibria for the three component system. The system had two liquid phases. The still was designed for use with two liquid phases. Also, with this still, no difficulty was encountered by having resorcinol freeze out while making the runs. The still was charged with 300 gm. mixtures with varied proportions of resorcinol to xylene. The per cent of resorcinol was held constant for a set of runs in which the proportions of p-xylene and o-xylene were varied. The concentrations of resorcinol used were twenty, forty, and ninety per cent of the total weight. The pressure over the liquid was held constant at one atmosphere with the Cartesian Manostat. This system required a much larger flame than did the Othmer still system. As soon as the condensing vapor interface reached the top of the flask neck, air was removed from the recycle system by opening the stopcock to the atmosphere for

a fraction of a second. Vapors were then allowed to condense in the vertical condenser and return to the still pot through the return tube. Ten minutes of boiling and recycling was sufficient for the vapors to reach equilibrium with the liquid in the pot. Vapors were then collected for analysis by shutting the two-way stopcock. Liquid for analysis was removed after the pot cooled down. The xylene mixture was pipetted from the cool solid-liquid mixture in the pot. An amount of pure xylene was added to the pot to restore its net weight to 300 gm. In the system with ninety per cent resorcinol there was not enough xylene in the liquid phase to allow removing it from the still after cooling, so the composition of the liquid in the still pot was calculated. The amount of pure xylene to be added to the still was equal to the amount of vapor sample collected.

## RESULTS

General:

The results of experimentation are tabulated in Tables VI through X. Table VI is a smoothed tabulation of all the equilibrium vapor-liquid compositions. All compositions are on a resorcinol-free basis. Table VII is a tabulation of the vapor-liquid equilibrium data for the paraxylene - orthoxylene system. It includes the temperatures at which the data were taken. Tables VIII-X include the data for the system o-xylene, p-xylene, and resorcinol at various concentrations of resorcinol in the liquid phases. All xylene concentrations are, again, on the resorcinol-free basis.

Figure 10 is an x-y diagram for the system at various concentrations of resorcinol in the liquid phase. Figures 11-14 are boiling point diagrams for the systems. All data were taken at a pressure of 760  $\pm$  2.6 mm. Hg.

The data indicate that there is a definite increase in the relative volatility of p-xylene to o-xylene due to the addition of resorcinol. However, the increase in the relative volatility due to an increase in the resorcinol concentration is slight. This seems to be more the case in the p-xylene rich mixtures. The curves for 40 and 90 per cent resorcinol concentrations are nearly superimposed at higher concentrations of p-xylene.

FIGURE 10

X - Y DIAGRAM FOR THE SYSTEM  
 ORTHOXYLENE - PARAXYLENE-  
 RESORCINOL AT 760 mm. Hg

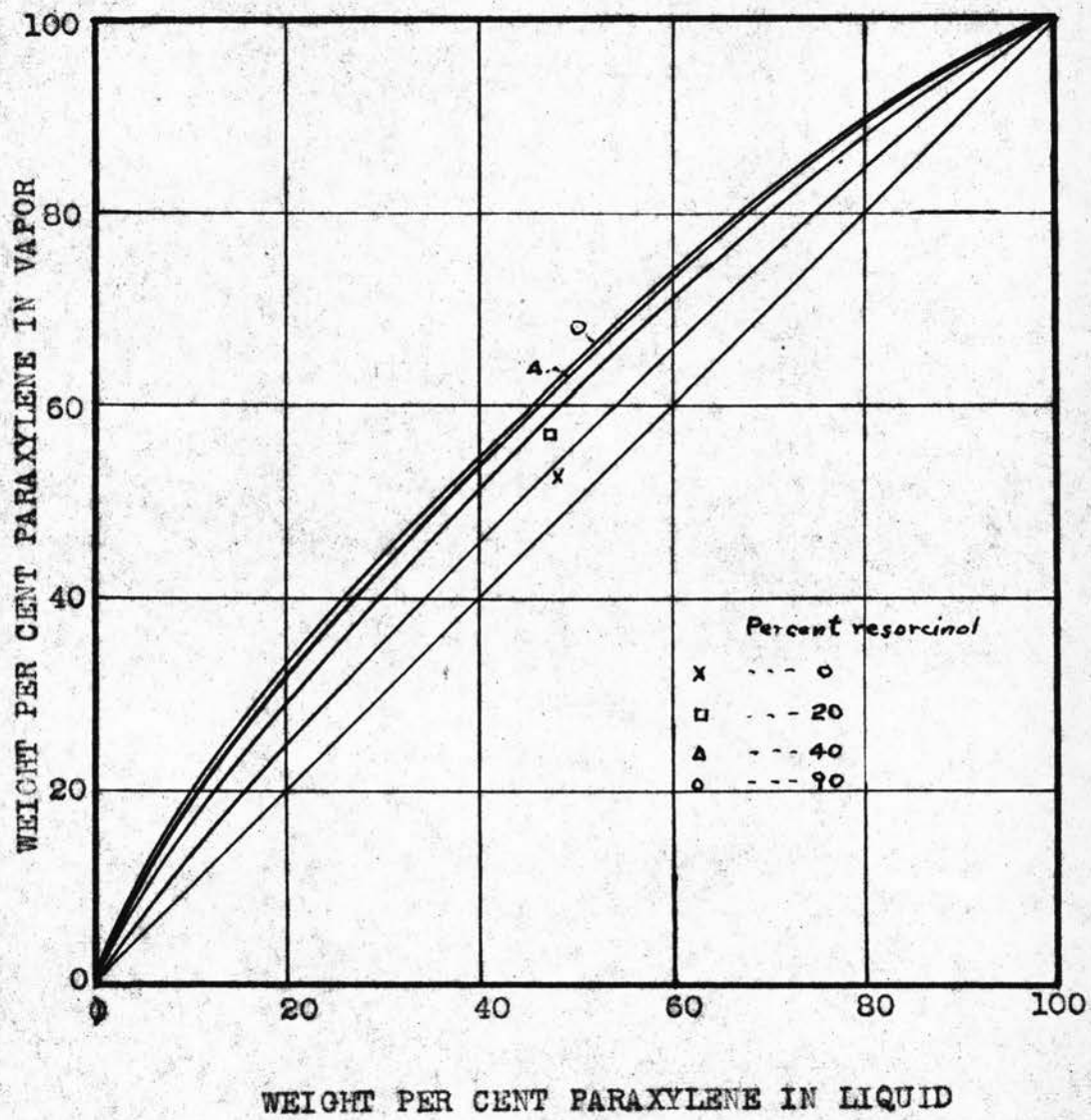




FIGURE 11

BOILING TEMPERATURE DIAGRAM FOR  
THE SYSTEM O-XYLENE - P-XYLENE AT 760 mm. Hg

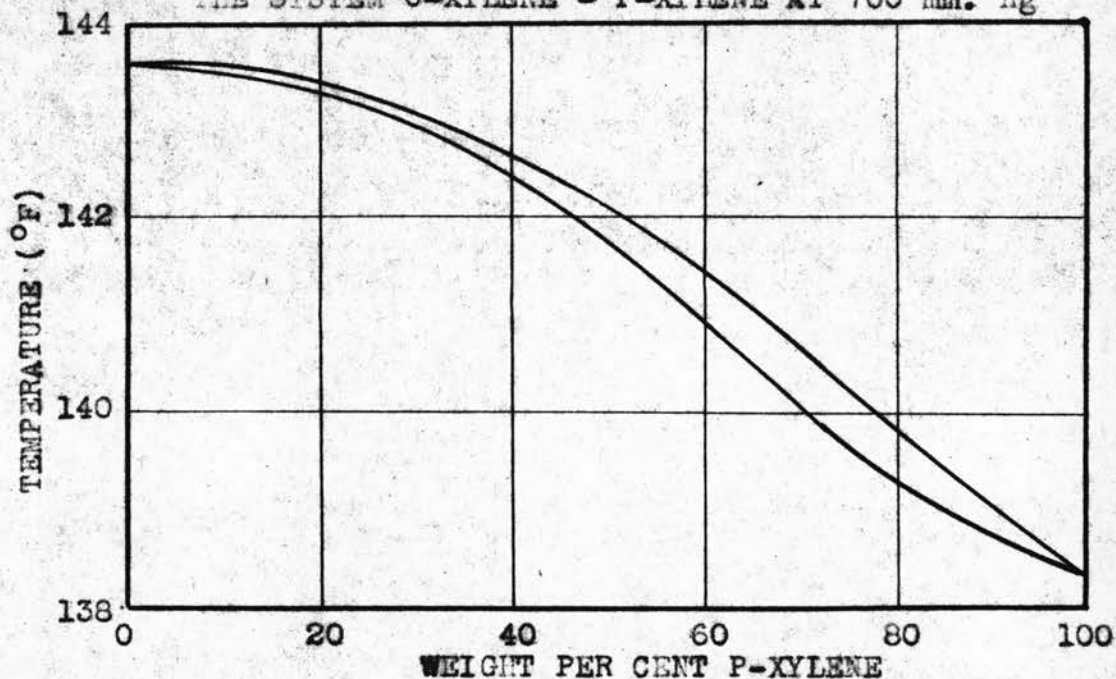


FIGURE 12

BOILING TEMPERATURE DIAGRAM  
FOR THE SYSTEM O-XYLENE - P-XYLENE  
20 PER CENT RESORCINOL AT 760 mm. Hg

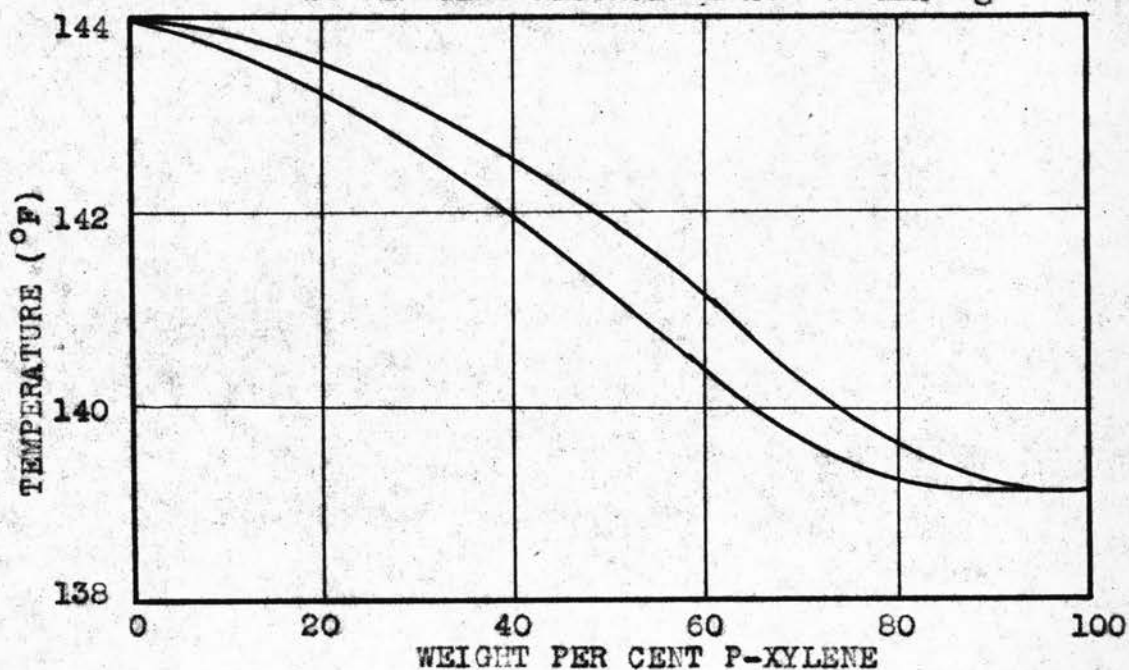


FIGURE 13

BOILING TEMPERATURE DIAGRAM  
FOR THE SYSTEM O-XYLENE - P-XYLENE  
40 PER CENT RESORCINOL AT 760 mm. Hg

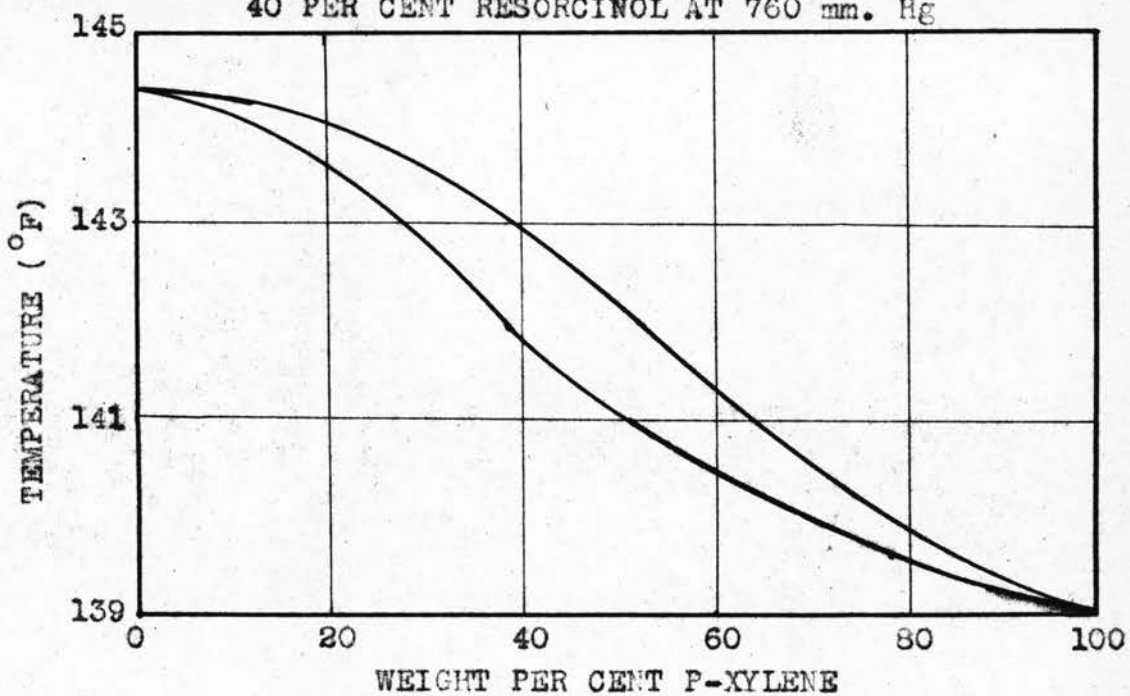
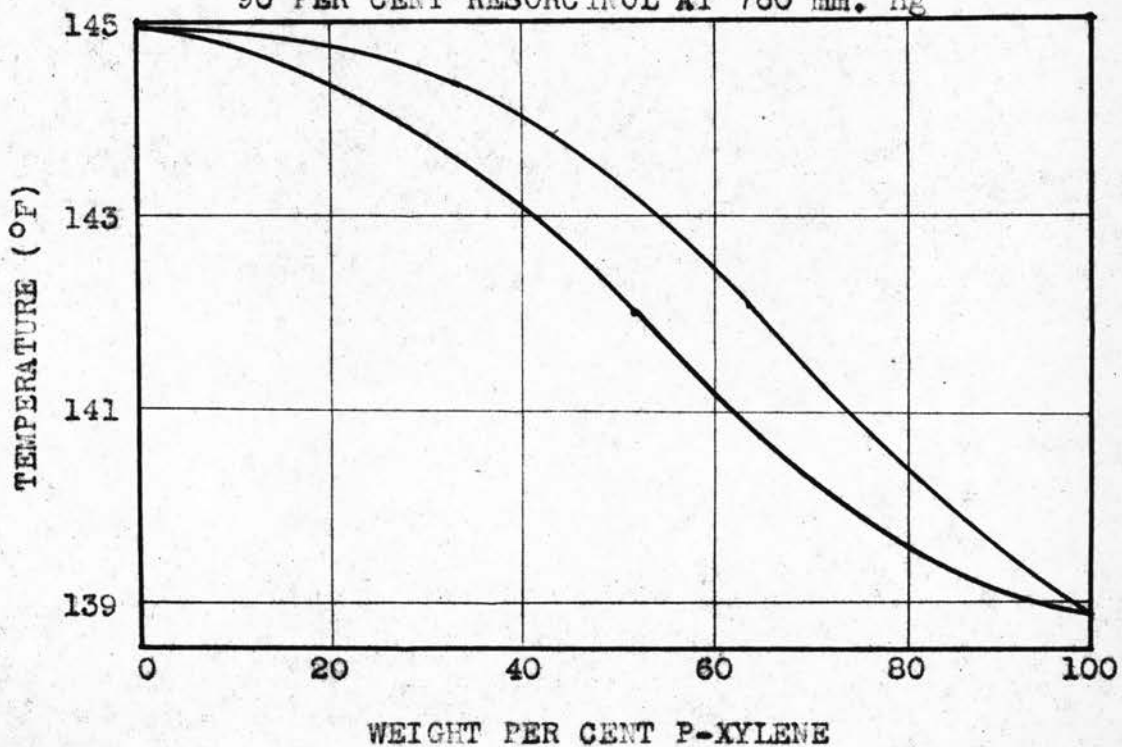


FIGURE 14

BOILING TEMPERATURE DIAGRAM  
FOR THE SYSTEM O-XYLENE - P-XYLENE  
90 PER CENT RESORCINOL AT 760 mm. Hg



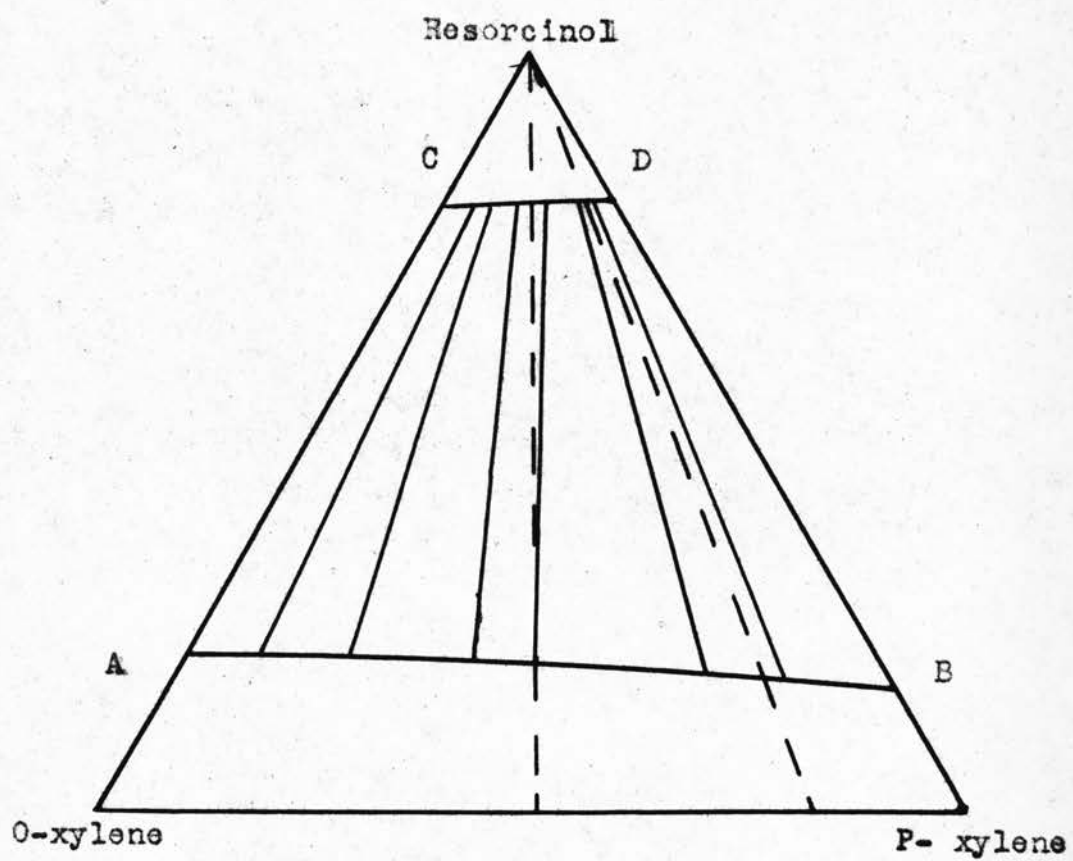
### Phase Relations:

A phase diagram for the system, orthoxylene - paraxylene - resorcinol was not determined. At room temperature the resorcinol is solid and only very slightly soluble in the xylenes. Data above the melting point of resorcinol was not accurate because of the high volatility of the xylenes at high temperatures. It would have been desirable to obtain data necessary for a complete analysis of phase relations at the high temperatures. However, use can be made of observations made during still runs and a phase diagram for the three component system can be sketched.

The system with 20 per cent resorcinol was very near to complete miscibility at its boiling points. The heavier resorcinol phase became very thin as the liquid was heated. The boiling liquid appeared to be clear but as soon as the heat was removed a very thin resorcinol phase appeared. The 40 per cent resorcinol mixtures were cloudy while boiling and the resorcinol phase which separated after the heat was removed was about one-third of the entire liquid phase. The 90 per cent resorcinol system was clear while boiling but a very thin layer of xylene seemed to remain on top of the resorcinol layer during the boiling. It is suspected that the 20 and 90 per cent resorcinol mixtures were very close to complete miscibility at their boiling temperatures. A phase diagram for the three component system at one atmosphere pressure and approximately 140° C. could look like that in Figure 15. This diagram affords an explanation of why there is little

FIGURE 15

PHASE DIAGRAM FOR THE THREE COMPONENT SYSTEM  
ORTHOXYLENE - PARAXYLENE - RESORCINOL



increase of relative volatilities with increased resorcinol concentrations. Line AB in Figure 15 indicates the approximate solubility of resorcinol in xylenes at temperatures near boiling. Line CD represents the approximate solubilities of xylene mixtures in resorcinol. Tie lines were not determined but could be closely represented by the solid lines connecting points on AB to points on CD. The dotted lines connecting points of zero per cent resorcinol with the one hundred per cent resorcinol apex represent points of constant paraxylene to orthoxylene ratios with varied resorcinol concentrations in the system. Since none of the tie lines cross each other their slopes will be very near those of corresponding dotted lines. The data indicate that these lines are nearly superimposed. Thus, any change in the resorcinol concentration for a given xylene mixture will have little effect on the composition of the two liquid phases represented by the ends of the tie lines.

#### Relative Volatility:

The relative volatility<sup>3,9</sup> of paraxylene to orthoxylene at various concentrations of resorcinol was determined. The relative volatility of the more volatile isomer to the less volatile compound is

$$\alpha = \frac{y_p \times x_o}{x_p \times y_o}$$

The relative volatility varies with different proportions of the xylenes as can be seen in Figure 16. In this figure parameters of resorcinol concentrations are shown. This

correlation gives a quick estimation of the effects of resorcinol concentrations on the separability of the two isomers. The greater the deviation of  $\alpha$  from unity, the greater is the ease of separation. As an example, the relative volatility of p-xylene to its isomer at 50 per cent p-xylene in the liquid is 1.25 with no resorcinol in the system. With 90 per cent resorcinol in the system this ratio is increased to 1.75 or 1.4 times as much.

#### Activity Coefficients:

The activity coefficient,  $\gamma^g$ , is used in this paper to show the deviations of solutions from the ideal behavior expressed by Raoult's law,

$$\pi y_1 = p_1 x_1$$

Thus, any deviations can be accounted for by placing the coefficient on the right side of this equation, and we have

$$\pi y_1 = \gamma_1 p_1 x_1$$

The deviation of any component from ideality varies with the concentration of that component in the liquid phase. As the concentration of a substance approaches purity the activity coefficient of that substance approaches unity. Gamma can be calculated for system whenever vapor-liquid equilibria data are available. The usefulness of this factor is found in correlation of data with empirical and semi-empirical equations (page 50). The activity coefficients for paraxylene and orthoxylene have been calculated from the data at various concentrations of resorcinol in the system. A plot of these

values is shown in Figure 18. The concentration of xylene is on the resorcinol-free basis. The coefficients of o-xylene and p-xylene at 20, 40, and 90 per cent resorcinol systems approach the value of the activity coefficient of the respective isomer in solution with resorcinol at the respective resorcinol concentrations. Figure 17 is a plot of activity coefficients of single xylene isomers in solution with resorcinol. Figure 17 shows that p-xylene deviates from ideal behavior more than does the o-xylene for all concentrations in resorcinol. Figure 18 shows that this same effect is present when both xylenes are in solution with resorcinol. The difference is even greater because each isomer tends to deviate more from ideality in its dilute solutions.

FIGURE 16

RELATIVE VOLATILITY OF  
P-XYLENE TO O-XYLENE

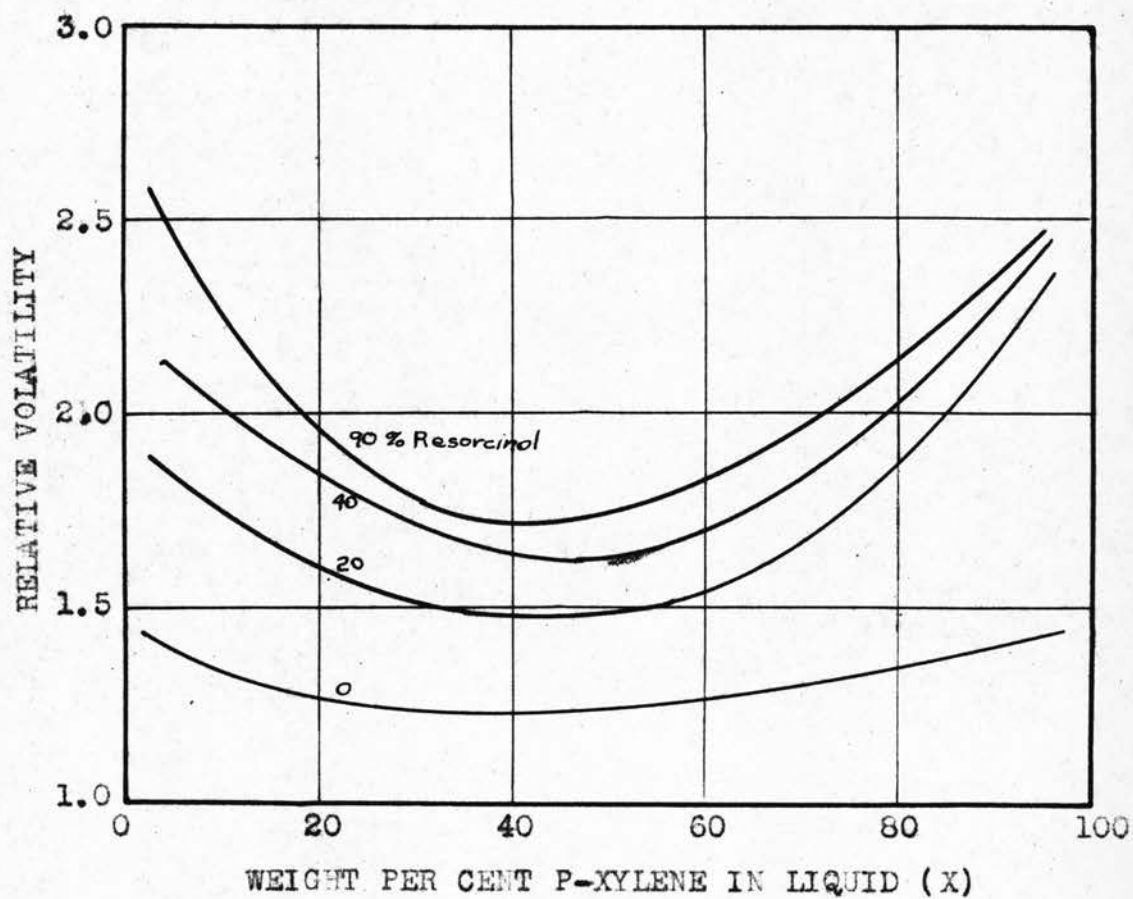




FIGURE 17

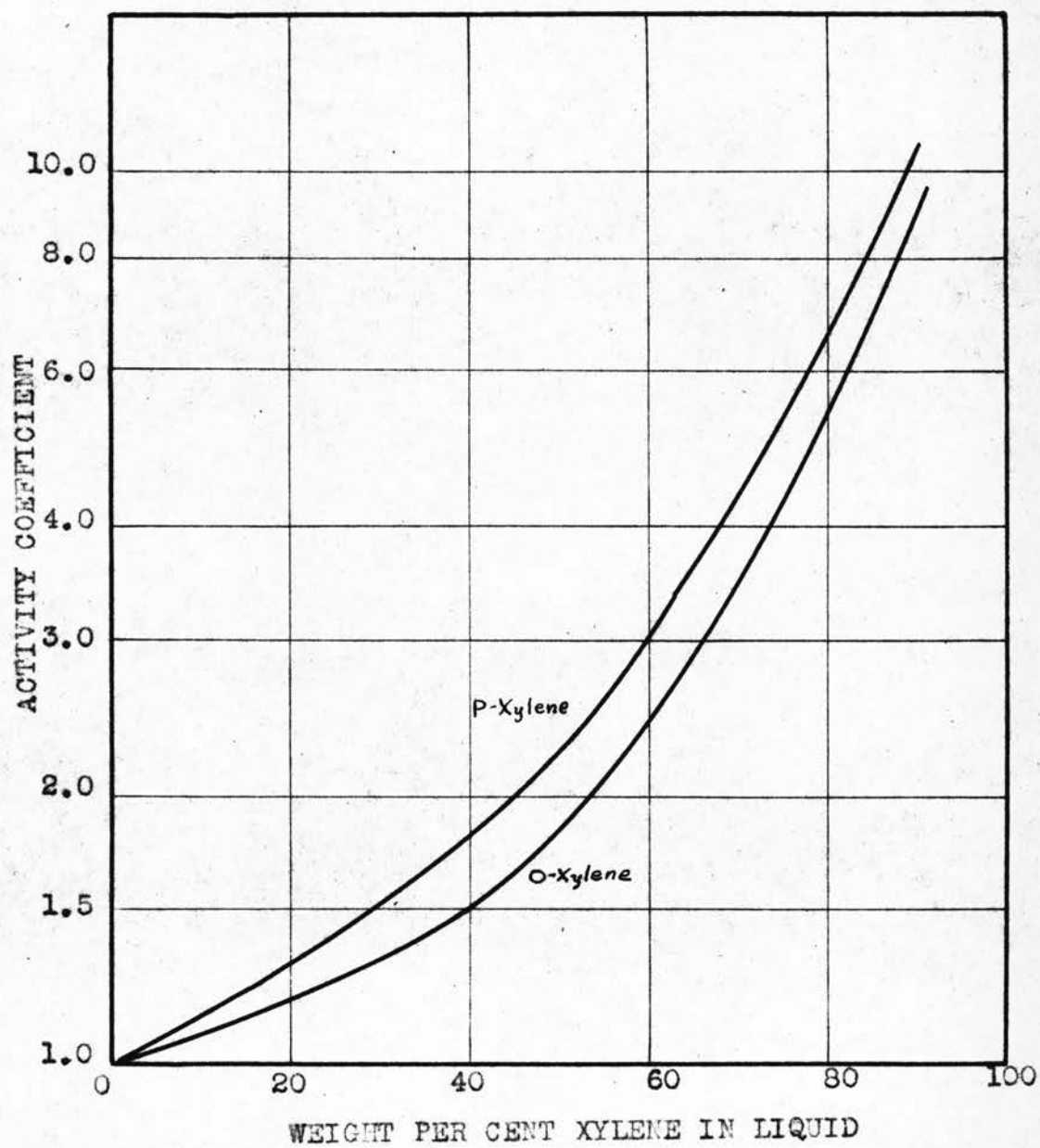
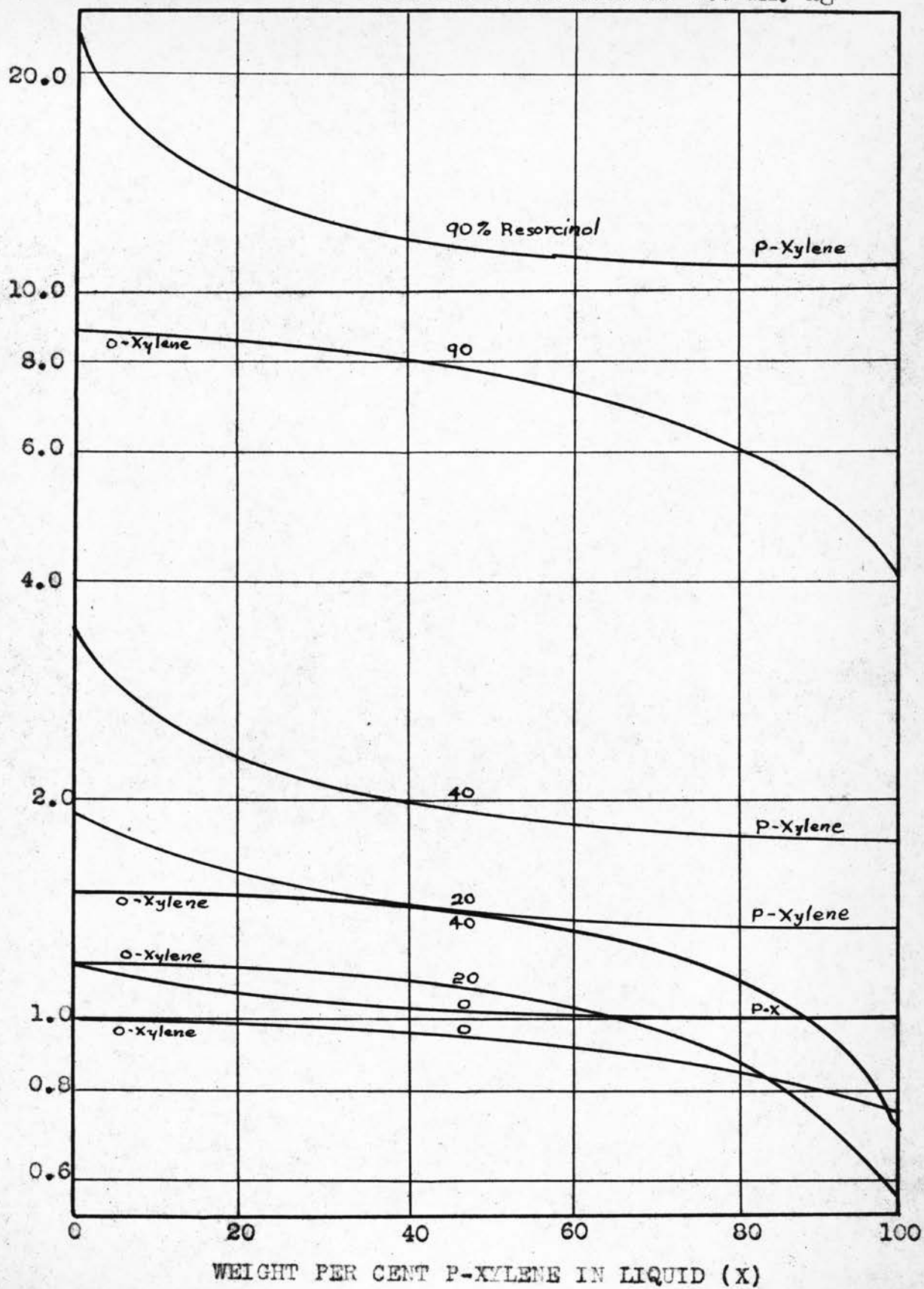
ACTIVITY COEFFICIENTS OF O-XYLENE  
AND P-XYLENE IN RESORCINOL SOLUTIONS

FIGURE 18

ACTIVITY COEFFICIENTS OF XYLENES AT 760 mm. Hg



## DISCUSSION

Resorcinol is shown to have positive effects upon the separation of paraxylene from orthoxylene. The effect is small and costs of the extractive distillation process would have to be compared with those of the ordinary distillation process now in use. The physical properties of metaxylene indicate that the separation of o-xylene from this compound would not be as pronounced as it is from the para isomer. The polarity of the meta isomer is 0.40 D while that of the ortho compound is 0.55 D and that for p-xylene is 0.0 D. It would seem that the deviations of o-xylene and m-xylene from ideal behavior will be more nearly the same than are the deviations of the ortho and para isomers in resorcinol solutions. Another factor which probably would decrease feasibility of separating the meta compound from the ortho isomer is the boiling point separation of these two compounds. Metaxylene boils at a slightly higher temperature than does the p-xylene. Thus, the relative volatility of m-xylene to o-xylene would be lower than the same relationship between the para and ortho isomers.

The most practical concentration of resorcinol in a distillation system with p-xylene and o-xylene is approximately 40 per cent. The increase of relative volatilities of the two compounds is not great enough at higher resorcinol concentrations to warrant use of those concentrations. Thirty-two theoretical trays are required for separation of the compounds to 99 per cent purity at zero resorcinol

concentration and at total reflux. The number of trays can be reduced to thirteen by adding resorcinol to a forty per cent concentration in the liquid.

Resorcinol fulfills many of the desirable qualities of an extractive agent. It is easily obtainable. Although it is expensive, it is not too unreasonable as far as cost is concerned. The compound is very soluble in water, a property particularly desirable since the melting point of resorcinol is so high. In the event that resorcinol lines were cooled down before the compound could be drained, water could be used to flush the lines out.

It would be desirable to obtain more equilibrium data for xylene systems. Data for a three component system including all of the xylene isomers as well as for the system of four components which would include resorcinol would be desirable. Data of this sort would be difficult to obtain. However, data for the systems metaxylene - orthoxylene and metaxylene - orthoxylene - resorcinol would be sufficient to determine the vapor-liquid equilibria for the four component system.

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## NOMENCLATURE

- A,B - Constants in Van Laar equation
- P - Vapor pressure
- X - Weight fraction of xylene in liquid phase on the resorcinol-free basis
- Y - Weight fraction of xylene in vapor phase on the resorcinol-free basis.
- Z - Weight fraction of resorcinol in liquid
- b,c - Constants in Margules' equation
- x - Weight fraction of component in liquid
- y - Weight fraction of component in vapor
- $\alpha$  - Relative volatility
- $\gamma$  - Activity coefficient
- $\mathcal{P}$  - Total pressure

Subscripts:

- m - Metaxylene
- o - Orthoxylene
- p - Paraxylene

## APPENDIX

TABLE III

Refractive Indices of Paraxylene -  
Orthoxylylene Solutions at 25° C.  
Abbe Refractometer

Experimental Data		Smooth Data	
<u>% P</u>	<u>Refractive Index</u>	<u>% P</u>	<u>Refractive Index</u>
0	1.5008	0	1.5008
30.3	1.4985	10	1.5000
36.8	1.4978	20	1.4992
58.6	1.4964	30	1.4985
60.8	1.4960	40	1.4977
67.6	1.4956	50	1.4969
86.0	1.4941	60	1.4961
87.0	1.4942	70	1.4954
100.0	1.4931	80	1.4946
		90	1.4939
		100	1.4931

TABLE IV

Scale Readings and Refractive Indices  
of Xylene Solutions with the Zeiss Refractometer  
at 24.8° C.

<u>% P-xylene</u>	<u>Refractive Index</u>	<u>Scale Reading</u>
0.0	1.5008	100.0
18.2	1.4988	93.5
41.1	1.4978	89.8
56.7	1.4968	86.0
75.0	1.4956	81.5
89.4	1.4946	77.9
100.0	1.4931	75.2

TABLE V

Deviations of Observed Values From  
Actual Values of Xylene Concentrations  
In the Equilibrium Still

<u>20% Resorcinol</u>		<u>40% Resorcinol</u>	
<u>% P - Observed</u>	<u>Actual % P</u>	<u>% P - Observed</u>	<u>Actual % P</u>
71.8	76.8	65.0	71.9
46.2	51.9	51.5	47.0
28.4	34.0		
15.3	21.3		
12.5	15.0		
77.0	82.5		
9.3	13.8		
1.5	2.0		



TABLE VI

Equilibrium Compositions of  
Vapor and Liquid for the  
System Orthoxylene - Paraxylene - Resorcinol  
At A Pressure 760 mm. Hg

X	Y			
	Z = 0	20	40	90
10	13.2	16.3	18.5	20.0
20	24.2	28.7	31.5	32.7
30	34.6	39.3	42.5	43.0
40	45.0	50.0	52.5	53.3
50	55.5	60.0	61.6	63.6
60	65.7	69.7	70.3	73.3
70	75.2	80.0	79.7	82.0
80	84.3	88.0	89.7	89.0
90	92.5	95.2	95.0	95.5

X = Wt. per cent of p-xylene in liquid, resorcinol-free basis

Y = Wt. per cent of p-xylene in vapor, resorcinol-free basis

Z = Wt. per cent of resorcinol in liquid phase

TABLE VII

Vapor-Liquid Equilibrium in the  
System Paraxylene - Orthoxylene  
at 760 mm.

<u>Experimental Data</u>			<u>Smoothed Data</u>		
<u>Temp.</u> <u>° C.</u>	<u>Wt. % Paraxylene</u>		<u>Temp.</u> <u>° C.</u>	<u>Wt. % Paraxylene</u>	
	<u>Liquid</u>	<u>Vapor</u>		<u>Liquid</u>	<u>Vapor</u>
143.6	0.0	0.0	143.6	0.0	0.0
143.6	10.0	13.2	143.5	10.0	13.2
143.5	21.1	25.5	143.3	20.0	24.2
143.0	33.2	37.3	142.9	30.0	34.6
142.0	43.0	47.7	142.4	40.0	45.0
141.7	50.0	55.5	141.8	50.0	55.5
141.0	55.5	61.2	141.1	60.0	65.7
140.5	65.5	71.2	140.3	70.0	75.2
140.0	77.5	82.5	139.4	80.0	84.3
139.0	84.4	88.0	138.6	90.0	92.5
138.4	90.7	93.0	138.3	100.0	100.0
138.3	100.0	100.0			

TABLE VIII

Vapor-Liquid Equilibrium  
In the System Paraxylene -  
Orthoxylene - Resorcinol at 760 mm.

Resorcinol in Liquid Twenty Weight Per Cent\*

<u>Experimental Data</u>			<u>Smoothed Data</u>		
<u>Temp.</u> <u>° C.</u>	<u>Wt. % Para*</u>		<u>Temp.</u> <u>° C.</u>	<u>Wt. % Para*</u>	
	<u>Liquid</u>	<u>Vapor</u>		<u>Liquid</u>	<u>Vapor</u>
143.7	12.0	19.7	143.7	10.0	16.3
143.2	17.5	28.3	443.2	20.0	28.7
143.0	26.0	35.7	142.6	30.0	39.3
142.5	34.0	43.0	141.9	40.0	50.0
142.0	41.0	50.5	141.1	50.0	60.0
141.0	50.0	59.2	140.3	60.0	69.7
141.0	52.5	62.0	139.7	70.0	80.0
140.5	55.0	65.7	139.2	80.0	88.0
140.2	57.0	66.7	138.8	90.0	95.2
140.0	65.4	76.7			
139.0	81.0	88.5			
139.0	88.8	94.0			

\* All percentages of paraxylene and orthoxylene are on the resorcinol-free basis.

TABLE IX

Vapor-Liquid Equilibrium  
In the System Paraxylene -  
Orthoxylene - Resorcinol at 760 mm.

Resorcinol in Liquid Forty Weight Per Cent\*

<u>Experimental Data</u>			<u>Smoothed Data</u>		
<u>Temp.</u> <u>° C.</u>	<u>Wt. % Para*</u>		<u>Temp.</u> <u>° C.</u>	<u>Wt. % Para*</u>	
	<u>Liquid</u>	<u>Vapor</u>		<u>Liquid</u>	<u>Vapor</u>
144.0	15.5	26.5	144.2	10.0	18.5
143.3	23.5	36.2	143.6	20.0	31.5
142.5	35.0	48.3	142.8	30.0	42.5
141.5	43.5	34.5	141.9	40.0	52.5
141.0	51.0	60.7	141.1	50.0	61.6
140.9	57.0	69.5	140.5	60.0	70.3
140.0	68.0	76.3	140.0	70.0	79.7
140.0	76.9	85.8	139.6	80.0	89.7
139.5	79.5	86.6	139.3	90.0	95.0
139.0	95.0	99.0			

\* All percentages of paraxylene and orthoxylene are on the resorcinol-free basis.

TABLE X

Vapor-Liquid Equilibrium  
In the System Paraxylene -  
Orthoxylene - Resorcinol at 760 mm.

Resorcinol in Liquid Ninety Weight Per Cent\*

<u>Experimental Data</u>			<u>Smoothed Data</u>		
<u>Temp.</u> <u>° C.</u>	<u>Wt. % Para*</u>		<u>Temp.</u> <u>° C.</u>	<u>Wt. % Para*</u>	
	<u>Liquid</u>	<u>Vapor</u>		<u>Liquid</u>	<u>Vapor</u>
144.8	9.9	20.0	144.8	10.0	20.0
144.0	22.5	35.5	144.4	20.0	32.7
143.9	31.9	42.0	143.8	30.0	43.0
143.0	43.8	50.0	143.1	40.0	53.3
141.7	53.2	66.8	142.2	50.0	63.6
140.5	61.1	74.4	141.1	60.0	73.3
140.0	73.5	83.6	140.3	70.0	82.0
140.0	80.5	89.3	139.5	80.0	89.0
139.5	84.7	92.5	139.1	90.0	95.5

\* All percentages of paraxylene and orthoxylene are on the resorcinol-free basis.

Physical Properties:

## (Xylenes)

Some of the properties of the xylenes are listed in Table XI below. All data except the dipole moments were obtained from Timmerman's "Physico-Chemical Constants of Pure Organic Compounds" (1950). The dipole moments were found in Water's "Physical Aspects of Organic Chemistry" (1950).

TABLE XI

Physical Properties of Xylenes

## Metaxylene

Boiling point ( $^{\circ}$ C.)	139.091	(Wojciechowski - 1939)
Freezing point ( $^{\circ}$ C.)	-47.89	(White and Rose - 1932)
Density (gm./cc.)	0.8600*	(Perkin - 1896)
Refractive index	1.49467*	(White and Rose - 1932)
Dipole moment	0.40 D	

## Orthoxylene

Boiling point ( $^{\circ}$ C.)	144.4	(Stuckey and Saylor - 1940)
Freezing point ( $^{\circ}$ C.)	-25.22	(Gibbons - 1946)
Density (gm./cc.)	0.87583	(Forziati, Glasgow - 1946)
Refractive index	1.50282	(Forziati - 1946)
Dipole moment	0.55 D	

## Paraxylene

Boiling point ( $^{\circ}$ C.)	138.348	(Forziati - 1946)
Freezing point ( $^{\circ}$ C.)	13.28	(Gibbons - 1946)

TABLE XI  
(continued)

Physical Properties of Xylenes

Paraxylene

Density (gm./cc.)	0.8567	(Williams and Krchna - 1927)
Refractive index	1.49319	(Forziati - 1946)
Dipole moment	0.0 D	

\* All data for densities and refractive indices were taken at a temperature of 25.0° C.

(Resorcinol)

The following data were obtained from Kirk and Othmer's "Encyclopedia of Chemical Technology" - 1953:

Boiling point	281.4° C.
Freezing point	109.8° C.
Dipole moment	2.07 D

This chemical should be kept in light resistant, dry, cool places to prevent decomposition. It is very hygroscopic. U.S.P. assay is 99.5 per cent resorcinol. Standard tests for purity are listed below.

1. A solution (1 in 20) of resorcinol in water is neutral or acid to litmus paper.
2. One gram of resorcinol is soluble in 1 ml. water.
3. Melting range is 109 to 111° C.
4. On drying over sulfuric acid for four hours it will not lose more than 1 per cent by weight.
5. A solution (1 in 20) in water gives no odor of phenol when heated.

6. Absence of pyro-catechol is shown by negative results with the lead acetate test.

Thermometers:

(Calibration Thermometer)

A National Bureau of Standards liquid in glass thermometer was used to calibrate the Zeiss thermometer which was used with the constant temperature bath. The nomenclature for the standard thermometer is as follows:

N. B. S. 93071

Bureau File 3.1

Test Number 117074

Calibration of Standard Thermometer

Reading ( $^{\circ}$ F.)	Temperature ( $^{\circ}$ F.)
67.00	66.91
72.00	71.90
77.00	76.88
82.00	81.89
87.00	86.83
92.00	91.83
97.00	96.81
102.00	101.78

(Zeiss Instrument Thermometer)

The thermometer used in conjunction with the Zeiss Refractometer was made in Germany:

Immersion	15 cm.
Mid-temperature	$20^{\circ}$ C.
Range	$10^{\circ}$ - $30^{\circ}$ C.



(Boiling point thermometer for  
three component system)

The thermometer used to measure temperatures in the Hands and Norman still was a Sargent thermometer. It was made in the U.S.A.

Immersion      76 mm.  
Range            -20° to 360° C.

Empirical Equations:

Correlation of the data was attempted with two accepted sets of equations. The first was Margules' empirical equations,<sup>9</sup> which can be written in the following form:

$$\frac{\ln \frac{\gamma_p}{x_o^2}}{x_o} = b + cx_o$$

$$\frac{\ln \frac{o}{x_p^2}}{x_p} = b + c (0.5 + x_o)$$

When the values on the left hand side of the equation are plotted against  $(x_o)$  and  $(x_o + 0.5)$  respectively, straight lines with a slope equal to  $c$  and an intercept equal to  $b$  should be formed. The constants,  $c$  and  $b$ , can be solved for directly from the equations if one experimental value is known. In the case of this thesis, however, there is no correlation with these equations. This is chiefly due to the fact that the activity coefficients are so close to unity that small experimental errors are greatly magnified when logarithms of the activity coefficient are used.

The second set of equations used was that of Van Laar.<sup>9</sup> These equations are semi-empirical, that is, they have a

derivation based on the thermodynamics of solutions but certain assumptions have been made to simplify the form of the equations. In their forms which are used for graphical solutions of the constants the Van Laar equations are as follows:

$$\frac{1}{\sqrt{T \ln \gamma_p}} = \frac{1}{\sqrt{B}} + \left( \frac{A}{\sqrt{B}} \right) \frac{x_p}{x_o}$$

$$\frac{1}{\sqrt{T \ln \gamma_o}} = \sqrt{\frac{A}{B}} + \left( \frac{1}{\sqrt{AB}} \right) \frac{x_o}{x_p}$$

Plots of the left hand terms against  $(x_p/x_o)$  or  $(x_o/x_p)$  should yield two straight lines which are closely related. For this system, however, straight lines were not obtained for the same reason the Margules equation failed. Values of A and B were calculated individually at different proportions of the xylenes in the two component system. They were of the same magnitude but the percentage error was quite large.

## SAMPLE CALCULATIONS

Concentration of p-xylene in liquid phase of the three component system containing 90 per cent resorcinol in the liquid phase:

(Data)

Weight of vapor sample = 4.4423 gm.  
 Per cent p-xylene in vapor = 35.5  
 Weight of xylene in liquid at start = 30.0 gm.  
 Per cent p-xylene in liquid at start = 23.6  
 Weight of p-xylene in liquid at start = 7.066

(Calculations)

Weight of p-xylene in vapor sample

$$0.355 \times 4.442 = 1.578 \text{ gm.}$$

Weight of xylene in liquid after run

$$30.0 - 4.44 = 25.56 \text{ gm.}$$

Weight of p-xylene in liquid after run

$$7.066 - 1.578 = 5.488 \text{ gm.}$$

Weight per cent of p-xylene in liquid after run

$$5.488 / 25.56 \times 100 = 21.5$$

Average per cent of p-xylene in liquid

$$\frac{23.6 + 21.5}{2} = 22.5$$

4.442 gm. of p-xylene were added to the still pot to bring the total weight of xylene back to 30.0 gm.

Weight of p-xylene in liquid

$$4.442 + 5.488 = 9.930 \text{ gm.}$$

Weight per cent of p-xylene in liquid at start of next run

$$9.930 / 30.0 \times 100 = 33.1\%$$

Relative Volatility:

Basis: Run I, two component system

(Data)

$$y_p = 0.132$$

$$y_o = 0.868$$

$$x_p = 0.100$$

$$x_o = 0.900$$

(Calculations)

$$\alpha = \frac{y_p x_o}{x_p y_o} = 1.368$$

Activity Coefficient:

Basis: Run I, two component system

(Data)

$$\text{Temperature} = 143.6^\circ \text{C.}$$

$$y_p = 0.132$$

$$x_p = 0.100$$

$$P_p = 866 \text{ mm. Hg}$$

(Calculations)

$$\gamma_p = \frac{\pi y_p}{P_p x_p} = 1.160$$

## VITA

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candidate for the degree of  
Master of Science

Thesis: A STUDY OF THE EFFECTS OF RESORCINOL  
ON THE VAPOR-LIQUID EQUILIBRIA OF THE  
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Date of Final Examination: August, 1954

THESIS TITLE: A STUDY OF THE EFFECTS OF RESORCINOL  
ON THE VAPOR-LIQUID EQUILIBRIA OF  
THE SYSTEM PARAXYLENE - ORTHOXYLENE

NAME OF AUTHOR: ROBERT L. KENDIG

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